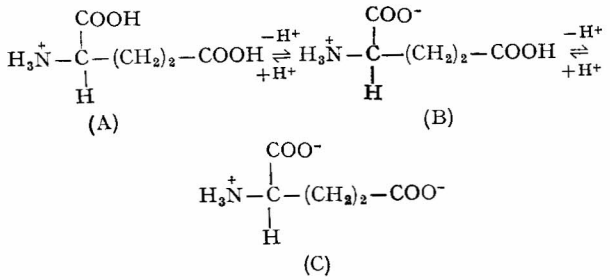
ponding decrease in diffusion current constant and half-wave potential (Table 2). From these results it is concluded that glutamic acid in 1% DMSO should be in 'zwitterion' form (B) and its reduction in acidic aqueous media[8,5] proceeds by following mechanism:



(A) (B) (C)

The above mechanism suggests that L-glutamic acid being a bifunctional acid, two electrons are involved in the reduction process. The values of diffusion current constant given in Table 2 in various supporting electrolytes also support that glutamic acid reduction proceeds by a two-electron process.

In 100% DMSO, Purdy *et al.*[3] have reported two waves of equal length each representing one electron process. It appears that these waves might coalesce and a single wave may be formed in aqueous solution probably due to the rapid conversion of (A) to (B), i.e. formation of zwitterions in aqueous solution. The carboxyl group adjacent to the α-amino group is reduced first very rapidly due to the proximity of charged (N^+H_3) and before reaching its limiting current potential value[10], the reduction of another carboxyl group starts resulting in the coalescence of the two waves into one.

Solution (5 ml) of $8\times10^{-4}M$ glutamic acid in $0{\cdot}1M$ $NaClO_4$, 0·002% Triton-x-100 at a limiting current value potential (1·54 V) was electrolysed under nitrogen atmosphere. A cathodic wave was obtained before, after 2 hr and after 6 hr electrolysis of the above solution. The changes in $E_{1/2}$ and i_d are summarized below:

	$-E_{\frac{1}{2}}$ (V)	i_d (μA)
Before electrolysis	1·3385	5·60
After 2 hr electrolysis	1·3415	4·70
After 6 hr electrolysis	1·3570	3·00

Increase in $-E_{\frac{1}{2}}$ after electrolysis supports the irreversible nature of the electrode reaction.

The decrease in i_d is due to decrease in the rate, at which the electroactive species diffuse into the electrode surface as electrolysis is prolonged[11].

Since the reduction of L-glutamic acid ($8\times10^{-4}M$) in 1% DMSO is irreversible, it is considered expedient to determine the values of transfer coeficient (α) and formal rate constant ($K^\circ_{f,h}$) for the electrode reaction by applying Koutecky's[12] theoretical treatment as extended by Meites and Israel[13] and tabulated below. The value of αn was obtained by equating the slope of $E_{d.e}$ vs log $[(i/i_d-i)-0{\cdot}546 \log t]$ plot to $-0{\cdot}0542/\alpha n$ and the intercept of the same plot giving $E_{1/2}$ was used to calculate $K^\circ_{f,h}$ from Eq. (1).

$$E_{1/2}=-0{\cdot}2412+\frac{0{\cdot}05915}{\alpha n}\log\frac{1{\cdot}349\times K^\circ_{f,h}}{D_{1/2}} \quad \ldots(1)$$

TABLE 2 — EFFECT OF VARYING DMSO CONCENTRATION ON DIFFUSION CURRENT CONSTANT

% DMSO in water	Diff. current constant (I)	$E_{\frac{1}{2}}$ (V)
01·0	4·087	1·3765
11·0	3·065	1·2570
21·0	2·578	1·2270
31·0	1·946	1·2145
41·0	1·411	1·2060
51·0	0·925	1·2050

TABLE 3 — VALUES OF THE VARIOUS KINETIC PARAMETERS

Temp. (°C)	$K^\circ_{f,h}$	αn	$-E^\circ_{1/2}$ (V)
30	$10{\cdot}36\times10^{12}$	0·452	1·370
40	$16{\cdot}69\times10^{-13}$	0·502	1·351
50	$43{\cdot}81\times10^{-14}$	0·542	1·333

The sign and meaning of the terms are same as described earlier[14]. The values of the kinetic parameters at different temperatures are given in Table 3.

It was observed that with increase in temperature, the value of $E^\circ_{1/2}$ shifts towards more positive values, showing the easier reduction which supports the irreversible nature of the electrode reaction.

The enthalpy of activation (ΔH) for the electrode reaction has been calculated by equating the slope of log $K^\circ_{f,h}$ vs 1/T plot to $(-\Delta H/2{\cdot}303)R$ and was found to be 8·50 kcal/mole.

References

1. DAYAN, V. H., *Diss. Abstr.*, **14** (1954), 1906.
2. OKAZAKI, Y. & OTSUKI, T., *Rev. Polarog. (Kyoto)*, **14** (1967), 307.
3. KOCH, T. R. & PURDY, W. C., *Analyt. chim. Acta*, **54** (1971), 271.
4. MEITES, L., *Polarographic techniques* (Interscience, New York), 1965, 141.
5. MATSUYAMA, G., *Polarographic studies of some substituted quinones*, Ph.D. thesis, University of Minnesota, 1948.
6. DAY, M. C. & SELBIN, J., *Theoretical inorganic chemistry* (Reinhold, New York), 1966, 335.
7. LI, C. & DOODY, EDWARD, *J. Am. chem. Soc.*, **74** (1952), 4184.
8. ADAMS, E. Q., *J. Am. chem. Soc.*, **38** (1916), 1503.
9. BJERRUM, N., *Z. phys. Chem.*, **104** (1923), 147.
10. CONN, E. & STUMFT, P. K., *Outlines of biochemistry* (John Wiley, New York), 1965, 68.
11. MEITES, L., *Polarographic techniques* (Interscience, New York), 1965, 112.
12. KOUTECKY, J., *Colln. Czech. chem. Commun.*, **18** (1953), 597.
13. MEITES, L. & ISRAEL, Y., *J. Am. chem. Soc.*, **83** (1961), 4903.
14. SAXENA, R. S. & SHEELWANT, S. S., *Indian J. Chem.*, **11** (1973), 43.

Polarographic Behaviour of Cu^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+} & Mn^{2+} Ions in Tris(hydroxymethyl)-methylamine & Their Simultaneous Determination in Ternary Mixtures

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A polarographic method has been developed for the simultaneous quantitative determination of metal ions in their ternary mixtures: (i) Cu^{2+}, Zn^{2+}, Mn^{2+}; (ii) Cu^{2+},

Cd^{2+}, Zn^{2+} and (iii) Cu^{2+}, Ni^{2+}, Zn^{2+}. Tris(hydroxymethyl)methylamine (0·5*M*) is used as a complexing agent in the determination of individual and mixtures of metal ions at *p*H 10·5 and μ=0·1*M*. Polarograms of both individual and mixtures of metal ions are well-defined and separated.

ONLY a few methods are described in literature for the simultaneous polarographic determinations of copper, cadmium, nickel, zinc and manganese ions. Zuliani and Pozzo[1] determined Cu^{2+}, Zn^{2+} and Mn^{2+} ions in the presence of iron and nickel. Jezdinsky[2] estimated Cu^{2+}, Ni^{2+} and Zn^{2+} ions using a base solution containing Tiron and KCN. Skobets and Povkhan[3] determined Cu^{2+}, Cd^{2+} and Zn^{2+} ions in ammonium acetate medium by oscillographic polarography. Nitric acid (1*M*)[4] and molten ammonium formate[5] have been used for determination of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+}. Wolff and Nuernberg[6] used a radiofrequency method for analysis of several mixtures. The polarographic behaviour of Cu^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+} and Mn^{2+} ions individually and of their mixtures, viz. Cu^{2+}, Zn^{2+}, Mn^{2+}; Cu^{2+}, Cd^{2+}, Zn^{2+}; and Cu^{2+}, Ni^{2+}, Zn^{2+} in tris(hydroxymethyl)methylamine has been investigated and methods developed for their simultaneous quantitative determination in mixtures.

All the chemicals used were of reagent grade. Conductivity water was used in the preparation of all solutions. Metal ion solutions were prepared from AR samples. The ionic strength was kept at 0·1 by adding the requisite amount of potassium nitrate (AR grade). Tris(hydroxymethyl)methylamine was a BDH sample. The polarograms of the deaerated solutions were recorded at 25° ± 0·1° with photographic polarograph system, Heyrovsky LP55. The potentials were measured against the saturated calomel electrode using agar-KNO_3 bridge. *p*H measurements were made using Elico *p*H model LI-10. Doubly distilled mercury was used for dme. The resistance measured by a conductivity bridge was less than 500 ohms and, therefore, no correction was made for *iR* drop.

The half-wave potentials of the ions shifted to more negative values with increasing [Tris] (0·5 to 2·0*M*) and increasing *p*H values. The reduction waves remained well-defined at all [Tris] and *p*H studied. The half-wave potentials in 0·5*M* Tris in the *p*H range 9 to 12·0 are reported in Table 1.

A series of polarograms were recorded with different aliquots of metal ions in 0·5*M* 'tris' at *p*H ~10·5. When the diffusion current was plotted against the metal ion concentration, linear plots were obtained indicating the feasibility of this

TABLE 1 — EFFECT OF *p*H ON HALF-WAVE POTENTIALS
{μ(KNO_3)=0·1*M* [Tris]=0·5*M*; [metal ion]=1 *mM*}

*p*H	$E_{\frac{1}{2}}$ — (V) vs SCE				
	Cu^{2+}	Cd^{2+}	Ni^{2+}	Zn^{2+}	Mn^{2+}
9·0	0·336	0·723	1·037	1·205	1·634
10·0	0·392	0·736	1·045	1·224	1·642
10·5	0·420	0·745	1·080	1·280	1·655
11·0	0·437	0·766	1·095	1·298	1·665
11·5	0·462	0·786	1·121	1·324	1·672
12·0	0·490	0·810	1·145	1·376	1·678

TABLE 2 — ANALYSIS OF TERNARY MIXTURE CONTAINING Cu^{2+}, Zn^{2+} AND Mn^{2+}

{[Tris]=0·5*M*; *p*H~10·5}

Cu^{2+} (mg)		Zn^{2+} (mg)		Mn^{2+} (mg)	
Taken	Found	Taken	Found	Taken	Found
1·5252	1·5252	0·5228	0·5242	0·5500	0·5500
1·6523	1·6364	0·7842	0·7768	0·5500	0·5500
1·5887	1·5887	0·9802	0·9802	0·6600	0·6680

TABLE 3 — ANALYSIS OF TERNARY MIXTURE CONTAINING Cu^{2+}, Cd^{2+} AND Zn^{2+}

{[Tris]=0·5*M*; *p*H~10·5}

Cu^{2+} (mg)		Cd^{2+} (mg)		Zn^{2+} (mg)	
Taken	Found	Taken	Found	Taken	Found
1·2708	1·2668	1·6860	1·6860	0·7840	0·7842
1·2708	1·2708	1·3500	1·3500	1·3076	1·3129
1·5885	1·5552	1·1240	1·1240	1·3076	1·3129
2·2242	2·2107	0·9000	0·9000	0·9149	0·9256

TABLE 4 — ANALYSIS OF TERNARY MIXTURE CONTAINING Cu^{2+}, Ni^{2+} AND Zn^{2+}

{[Tris]=0·5; *p*H~10·5}

Cu^{2+} (mg)		Ni^{2+} (mg)		Zn^{2} (mg)	
Taken	Found	Taken	Found	Taken	Found
1·2708	1·2708	0·8190	0·8190	0·6538	0·6484
1·5252	1·5252	1·1700	1·1790	0·7842	0·7792
1·2708	1·2708	2·1060	2·1060	0·9807	0·9807

method for the quantitative determination of the metal ion.

The effect of height of mercury column on i_d has been studied and the plot between i_d vs $\sqrt{h}$ is linear indicating diffusion-controlled limiting current of all these reductions. However, the log plots obtained gave values for slope different from those required for reversible reduction except in the case of cadmium. Hence these metals, except cadmium, are reduced irreversibly.

The $E_{\frac{1}{4}}$ values were well separated and in view, of the analytical applications of different metal ions in mixtures, different synthetic mixtures were prepared. The analysis of the following mixtures were carried out in pH ~10·5 using 0·5M tris and 0·1M KNO_3: (i) Cu^{2+}, Zn^{2+} and Mn^{2+} (Table 2); (ii) Cu^{2+}, Cd^{2+} and Zn^{2+} (Table 3); and (iii) Cu^{2+}, Ni^{2+}, and Zn^{2+} (Table 4). The results obtained are satisfactory.

References

1. Zuliani, G. & Dal Pozzo, P., *Metano (Padua)*, **14** (1960) 111.
2. Jezdinsky, R., *Chem. Zvesti.*, **16** (1962), 295.
3. Skobets, E. M. & Povkhan, M. F., *Ukr. Khim. Zh.*, **30** (1964), 792.
4. Dolezal, J., Beran, P. & Tvrzicka, E., *Colln. Czech. chem. Commun.*, **33** (1968), 2322.
5. Lyalikov, Yu. S., Novik, R. M. & Vassershstein, Sh. E., *Akad. Nauk Moldavsk. SSSR*, **9** (1963), 22.
6. Wolff, G. & Nuernberg, H. W., *Z. Analyt. Chem.*, **224** (1967), 332.

Reduction of Cd(II)-Itaconate & Cd(II)-Oxalate-Itaconate Complexes at d.m.e.

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Electrode reactions of Cd(II) with itaconate and with oxalate-itaconate as mixed ligand ions have been studied polarographically. Cadmium(II) forms three complexes with itaconate ions (ITA)$^{-}$ with their respective stability constants, in two different electrolytes (KNO_3 and $NaNO_3$) at ionic strength 2·5M, as follows: log β_1 = 1·73, 1·78; log β_2 = 2·36 ± 0·09, 2·30 ± 0·04; and log β_3 = 3·20 ± 0·05, 3·39 ± 0·07. Schaap and McMasters treatment points to the existence of three mixed ligand chelates having 1:1:1, 1:1:2 and 1:2:1 ratio of Cd(II)-Ox-ITA. The observed enhancement of the complexation constant of the mixed ligand chelates has been explained on statistical considerations and on the possibility of simultaneous n-bonding of Cd(II) with both the ligands.

THE formation of mixed ligand chelates of Nd^{3+} and VO^{2+} with itaconate and phenolic acids were investigated potentiometrically in this laboratory[1,2]. In continuation of our earlier studies[3-7], we report here the polarographic determination of the formation constants of Cd(II) with itaconate and mixed ligand complex with oxalate.

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Reagents used were of AR grade. Potassium oxalate and potassium itaconate, at pH 7·0, were used as complexing agents. KNO_3 and $NaNO_3$ were used as supporting electrolytes and to maintain the ionic strength at 2·5M. The experimental technique was the same as described earlier[3,4].

DeFord and Hume's[8] method was applied to evaluate stability constants for the two-electron, reversible and diffusion-controlled reduction of Cd(II)-oxalate system at pH 7·0 and at ionic strength of 2·5M (KNO_3). The values came out to be log β_{10} = 2·70 ± 0·04, log β_{20} = 4·07 ± 0·15 and log β_{30} = 5·14 ± 0·06 and agreed well with those obtained by earlier workers[3,9-11].

In each solution of the system Cd(II)-itaconate, Cd^{2+} was 1 mM. The [ligand] was varied from 0·05 to 0·70M, and the ionic strength was adjusted to 2·5M by adding appropriate quantity of KNO_3. In a second set instead of KNO_3, the supporting electrolyte used was $NaNO_3$. A single well-defined reduction wave appeared in both the sets and the plots of i_d vs $\sqrt{h}$ (h = effective height of mercury column) were linear, passing through the origin. Again, as expected, the plot of i_d vs [metal ion] was linear. The results obtained showed that the reduction was diffusion-controlled. The plots of log i/i_d-i vs $E_{d.e.}$ were linear with slopes = 32 ± 1 mV, corresponding to reversible reduction with n = 2. The half-wave potential shifted continuously towards more negative values and the diffusion current decreased with increasing [ligand], indicating positively a complex formation of metal ion with the ligand.

Plots of $-E_{1/2}$ vs $-\log C_L$ (C_L = ligand concentration) were smooth curves pointing to the formation of two or more complex ions, in equilibrium. The DeFord and Hume[8] method, as modified by Irving[12], was used for calculating successive stability constants of various species. The values of overall log stability constants, as obtained from $F_{i0}[X]$ vs C_L curves for the complex species [Cd(ITA)], $[Cd(ITA)_2]^{2-}$ and $[Cd(ITA)_3]^{-4}$ are: 1·78, 2·30 ± 0·04, 3·39 ± 0·07 and 1·73, 2·36 ± 0·09, 3·20 ± 0·05 respectively at μ = 2·5M ($NaNO_3$ and KNO_3). The stability constants of Cd(II)-itaconate at μ = 2·5M (KNO_3) were used in the calculation of stabilities of mixed ligand systems, since the experimental conditions were identical in the both.

For the mixed ligand study the two concentrations of itaconate chosen were 0·08 and 0·24M at which 1:1 and 1:2 species predominated. Each solution contained 1 mM Cd^{2+}, 0·08M itaconate and only the oxalate concentration was varied from 0·02 to 0·50M. The ionic strength was adjusted to 2·5M by adding appropriate amount of KNO_3 at pH 7·0. The exact procedure was repeated for [itaconate] = 0·24M.

The plots of $-E_{d.e.}$ vs $\log i/(i_d-i)$ in the two sets studied were linear with the slope values lying in the range 30-32 mV, which clearly showed that the reduction of Cd(II) ion in the absence and presence of the ligands is reversible involving two electrons. That the reduction was diffusion-controlled was evidenced by the direct proportionality of diffusion current to the square root of the effective height of the mercury head.